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CRYSTAL CHEMISTRY OF THE BASIC MANGANESE ARSENATE MINERALS: II. THE CRYSTAL STRUCTURE OF ALLACTITE

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ABSTRACT

Allactite, $Mn_7(OH)_8(AsO_4)_2$, $a=11.03$, $b=12.12$, $c=5.51$ Å, $\beta=114°04'$, $Z=2$, $P2_1/a$, solved by vector sets applied to $P(xy)$ and $P(xz)$, is a complicated structure. $R_{hkl}=0.077$ for 838 independent reflections.

Its principal features are bands of octahedra, two octahedra wide, held together by vertex-linked octahedra, forming flat sheets parallel a $\{100\}$. These sheets are in turn held together by chains of linked Mn(2)-O octahedra and As-O tetrahedra running parallel b [010]. The bridging Mn(2)-O octahedra connect to the sheets in a complicated fashion, exhibiting corner-, edge-, and face-sharing with them.

Average distances are: Mn(1)-O 2.27, Mn(2)-O 2.23, Mn(3)-O 2.18, Mn(4)-O 2.19, and As-O 1.68 Å, all ±0.03 Å. One distance, Mn(2)-O(5) 2.59±0.03 Å, is abnormally long since O(5) is coordinated to four octahedra. Excluding this distance, the remaining twenty unique Mn-O distances have a maximum difference of 0.25 Å.

The octahedral bands are strips of the pyrochroite structure and it is suggested that this may be a dominant feature for other basic manganese arsenates as well.

INTRODUCTION

Allactite, $Mn_7(OH)_8(AsO_4)_2$, is a member of the homologous series of basic arsenates of manganese with general formula $Mn_n^{+2}(OH)^{-}_{2n-3z}(AsO_4)_z^{-3}$. This group of minerals is very local in occurrence and is restricted to low temperature hydrothermal vein systems associated with manganese-iron oxide orebodies of the pyrometasomatic type in dolomitic marbles. Noteworthy occurrences of these arsenates are in Sweden, including Östra Mossgruvan[1] and Jakobsberg in Nordmark, Långban, and Harstigen (near Filipstad) in the province of Värmland; and Sjögruvan (near Grythyttan) in the province of Örebro. The only other occurrence outside Sweden is Franklin and Sterling Hill, New Jersey where several basic arsenates occur upon cracks in franklinite-willemite-zincite ore in Mg-poor marbles.

At all these locations the basic manganese arsenates have a characteristic paragenesis. They usually occur in close association and have crystallized late with calcite, pyrochroite and barite. This type of close association is found also for other notable homologous series of anisodesmic oxysalts: the basic arsenates of copper, $Cu_n^{2+}(OH)_{2n-3z}(AsO_4)_z^{3-}$; the basic phosphates of copper, $Cu_n^{2+}(OH)_{2n-3z}(PO_4)_z^{3-}$; and the iron-manganese orthophosphate hydrates, $(Fe+Mn)_n^{2+}(OH)_{2n-3z}(H_2O)_r$

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[1] Gruva = mine.

$\cdot(PO_4)^{3-}_z$. Surveys on these interesting groups include a paper by Ghose (1966) for the copper compounds and one by Moore (1965) for the Fe-Mn phosphate hydrates.

The basic manganese arsenates are closely allied structurally to the basic arsenates and phosphates of copper, disregarding the Jahn-Teller distortions of the Cu^{+2} complexes. The crystal structures investigated so far reveal ribbons, bands, and incomplete sheets of vertex- and edge-linked distorted metal-oxygen octahedra held together in three dimensions by tetradentate $(AsO_4)^{3-}$ and $(PO_4)^{3-}$ tetrahedra.

Allactite is the most frequently observed of the basic manganese arsenates. The material used in this study came from a lovely group of pleochroic purplish-red to greyish-green crystals implanted upon calcite and associated with pyrochroite and synadelphite from Långban, Sweden.

EXPERIMENTAL

904 independent intensities from the *hk*0, *hk*1, *hk*2, and *h*0*l* levels were gathered on a manual Weissenberg geometry counter-diffractometer using Zr-filtered Mo radiation. The wedge-shaped crystal of 0.029 mm³ volume showed predominant *f* {210} and *v* {111}. Its surfaces were carefully measured and a polyhedral transmission correction was applied using a modified GNABS program of Burnham (pers. comm.).

The Patterson projections $P(xy)$ and $P(xz)$ were prepared as well as three-dimensional $P(xyz)$. Unfortunately, there were no data for the levels greater than $l=2$ with c as rotation axis and $P(xyz)$ was nearly unintelligible. The trial structure was deduced from the two projections.

I used the following data of Hurlbut in Palache, Berman, and Frondel (1960): $a=11.03$, $b=12.12$, $c=5.51$ Å, $\beta=114°04'$, $P2_1/a$. These data were confirmed in this study and diffractometer scans indicated that they are good to ± 0.02 Å on a and b and ± 0.01 Å on c.

SOLUTION OF THE STRUCTURE

The unit cell contains $Mn_{14}(OH)_{16}(AsO_4)_4$ and since the space group $P2_1/a$ is uniquely determined, the minimum equipoint rank number is 2, which is any set of inversion centers with no degrees of freedom. Thus Mn(1) was arbitrarily placed at $(000; \frac{1}{2}\frac{1}{2}0)$.

Consequently, $P(xy)$ has a superimposed *cmm* plane group due to $Mn(1)_{00}$-$(Mn,As)_{xy}$ and $(Mn,As)_{xy}$-$Mn(1)_{\frac{1}{2}\frac{1}{2}}$ pairs. Studying this subset on $P(xy)$ gave clues to some of the metal positions though the vector densities indicated that certain metal-metal vectors were either overlapping or the metals were in unusual relationship with each other (*i.e.* atomic coordinates 0y). In fact, several models were tested which fit $P(xy)$ fairly well and all yielded $R_{hk0} \sim 0.36$–0.40. Despite these encouraging discrepancy factors for metals only, all models were later proven to be incorrect.

The solution was found on $P(xz)$. Unusually strong vector density was located at $u=0$, $w=\frac{1}{2}$, and along with a rather simple map this could only be interpreted as two independent Mn atoms overlapping at $x=0$ and $z=\frac{1}{4}$ in crystal space. All other vectors were immediately labelled starting with $2Z_{\mathrm{Mn}(x=0,\ z=\frac{1}{4})}-Z_{\mathrm{Mn}(xz),\mathrm{As}(xz)}$ where Z is the atomic number. The discrepancy index, R_{h0l}, converged to 0.28 for metals only. This afforded an interpretation of ambiquities on $P(xy)$ and the correct model was soon found. R_{hk0} converged to 0.29 for metals only, whereupon a Fourier electron density map was prepared. All oxygen atoms were well-resolved on this map and their z-coordinates were calculated assuming Mn−O∼2.20 Å.

The difficulty of the crystal structure analysis for allactite is realized when the coordinates of two independent Mn atoms in general positions proved to be Mn(3)$\sim$0, 0.57,$\sim\frac{1}{4}$ and Mn(4)$\sim$0, 0.29,$\sim\frac{1}{4}$ respectively.

REFINEMENT

Scattering factor tables for Mn^{1+}, As^{3+}, and O^{1-}were prepared from International Tables, Vol. 3 (1962). Three cycles of coordinate refinement led to $R_{hkl}=0.148$, using the program ORFLS of Busing, Martin, and Levy (1962). Sixty-six reflections were then excluded from refinement: nine were very strong reflections showing severe extinction effects, seven were eclipsed by continuous radiation from neighboring strong intensities, seven were erroneous data, and the remainder were "zero intensities." Remaining were 838 reflections for full-matrix atomic coordinate and isotropic temperature factor refinement, and after three cycles all shifts were within their limits of error.

Including the sixty-six reflections, $R_{hkl}=0.122$. Excluding them, $R_{hkl}=0.077$. Table 1 lists the atomic coordinates and isotropic temperature factors for the thirteen atoms in the asymmetric unit of allactite structure. The $\mathrm{F_{obs}}$-$\mathrm{F_{calc}}$ data are presented in Table 2.[1]

DISCUSSION OF THE STRUCTURE

The main feature of the allactite structure includes symmetry equivalent levels of Mn-O open sheets parallel *a*{100} and Mn-O and As-O chains running parallel *b*[010].

The sheets are the most striking aspect of the structure as seen in Figures 1 and 2. They consist of edge-linked bands of Mn-O octahedra two octahedra wide held together in a plane by vertex-linked Mn(1)-O

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[1] Table 2 has been deposited as Document No. 9820 with the American Documentation Institute, Auxiliary Publications Department, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing the document number, and remitting in advance $1.25 for photoprints or $1.25 for 35 mm microfilm.

TABLE 1. ALLACTITE. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

	x	y	z	B
Mn(1)	0	0	0	1.30(6)
Mn(2)	0.2101(2)[a]	0.1801(3)	−0.0604(4)	0.96(4)
Mn(3)	− .0067(3)	.4308(3)	.7404(8)	0.82(5)
Mn(4)	− .0001(3)	.2893(3)	.2516(8)	1.02(5)
As	− .2079(1)	.0794(2)	.3262(3)	0.18(3)
O(1)[b]	.1152(13)	.3065(13)	.6733(36)	1.07(22)
O(2)	− .1219(11)	.5717(11)	.8256(35)	0.56(20)
O(3)[b]	.0938(13)	.1554(14)	.1726(26)	1.46(23)
O(4)	− .1660(14)	.2017(14)	.2525(28)	1.47(23)
O(5)[b]	− .1153(13)	.4373(13)	.3116(38)	1.36(26)
O(6)[b]	.1257(12)	.6831(12)	.1744(36)	0.92(22)
O(7)	− .1414(12)	− .0187(12)	.2131(24)	0.93(20)
O(8)	.3380(12)	.4259(14)	.6601(21)	1.36(20)

[a] Standard errors are given in parentheses.

[b] Hydroxyl groups.

octahedra at the cell origin. These octahedral bands are actually strips of the pyrochroite structure.

Between the sheets are chains of vertex-linked As-O tetrahedra and highly distorted Mn(2)-O octahedra which serve as the 'cement' for the sheets. The distorted Mn(2) octahedron plays a highly complicated role. It shares four vertices among six octahedra in the sheets, two vertices with the arsenate tetrahedra, one edge with the Mn(1) octahedra in the sheets, and a face with the Mn(4) octahedra in the sheets! This Mn(2) octahedron is singled out in Figure 3. It is remarkable that such a complicated arrangement is encountered in the most frequently observed member of the basic manganese arsenates. It may also be noted in Figure 1 that the Mn(2) octahedra by sharing edges with the Mn(1) octahedra make up a triple group in the structure.

There are a total of twenty-one independent Mn-O octahedral distances for allactite in Table 3. Excluding the Mn(2)-O(5) distance, these distances range from 2.06(Mn(4)-O(3)) to 2.31±0.03 Å (Mn(1)-O(7)) with a maximum difference of 0.25 Å. The averages are Mn(1)-O 2.27, Mn(2)-O 2.23, Mn(3)-O 2.18 and Mn(4)-O 2.19±0.03 Å. All these observations are representative of typical Mn^{2+}-O octahedral distances.

However, the Mn(2)-O(5) distance of 2.59±0.03 Å is unusually long. This is readily explained on the basis of Table 4. It is seen that the O(1), O(3), and O(6) hydroxyl oxygens are just saturated, according to Pauling's electrostatic valence bond rule. The O(5) hydroxyl is oversaturated since it is associated with four octahedra. Three of these

TABLE 3. ALLACTITE. INTERATOMIC DISTANCES

Mn-O octahedral distances

Mn(1)-O		Mn(2)-O		Mn(3)-O		Mn(4)-O	
2O(3)	2.300	1O(1)	2.085	1O(1)	2.149	1O(1)	2.155
2O(7)	2.314	1O(3)	2.173	1O(2)	2.288	1O(2)	2.302
2O(2)	2.185	1O(4)	2.230	1O(2′)	2.229	1O(3)	2.065
aver:	2.266 Å	1O(5)	2.591	1O(5)	2.181	1O(4)	2.115
		1O(6)	2.145	1O(5′)	2.171	1O(5)	2.299
		1O(7)	2.141	1O(6)	2.086	1O(6)	2.211
		aver:	2.227 Å		2.184 Å		2.191 Å

O-O edge distances for octahedra

Mn(1)		Mn(2)		Mn(3)		Mn(4)	
2O(3)-O(7)	2.973	O(1)-O(3)	3.391	O(2′)-O(1)	3.130	O(1)-O(2)	3.119
2O(3)-O(7′)	3.420	O(1)-O(4)	3.118	O(2′)-O(2)	3.119	O(1)-O(3)	3.237
2O(3)-O(8)	3.225	O(1)-O(6)	3.025	O(2′)-O(5)	3.133	O(1)-O(4)	3.278
2O(3)-O(8′)	2.930	O(1)-O(7)	3.535	O(2′)-O(6)	2.948	O(1)-O(5)	2.969
2O(7)-O(8)	3.198	O(3)-O(4)	3.043	O(5′)-O(1)	2.969	O(2)-O(3)	3.450
2O(7)-O(8′)	3.167	O(3)-O(7)	2.906	O(5′)-O(2)	3.266	O(2)-O(5)	3.005
aver:	3.152 Å	O(5)-O(3)	3.184	O(5′)-O(5)	2.962	O(4)-O(3)	3.122
		O(5)-O(4)	2.903	O(5′)-O(6)	3.229	O(4)-O(5)	2.903
		O(5)-O(6)	3.010	O(5) -O(1)	3.105	O(6)-O(2)	2.948
		O(5)-O(7)	3.084	O(5) -O(2)	3.007	O(6)-O(3)	3.094
		O(6)-O(7)	3.189	O(6) -O(1)	3.098	O(6)-O(4)	2.920
		O(6)-O(4)	2.920	O(6) -O(2)	3.088	O(6)-O(5)	3.010
		aver:	3.109 Å		3.088 Å		3.088 Å

O-O grand average: 3.109 Å

As-O tetrahedral distances		O-O edge distances for tetrahedra	
O(2)	1.718	O(2′)-O(7)	2.757
O(4)	1.652	O(2′)-O(8)	2.763
O(7)	1.647	O(4)-O(2′)	2.706
O(8)	1.698	O(4)-O(7)	2.702
aver:	1.679 Å	O(4)-O(8)	2.726
		O(7)-O(8)	2.799
		aver:	2.742 Å

Mn-Mn distances in pyrochroite fragment

Mn(3)-Mn(4)	3.392
Mn(3)-Mn(4′)	3.190
Mn(3)-Mn(4″)	3.298
Mn(3)-Mn(3′)	3.188
Mn(3)-Mn(3″)	3.266
	3.267 Å

Errors:

Mn-O ± .03 Å
As-O ± .03 Å
Mn-Mn ± .007 Å
O-O ± .05 Å

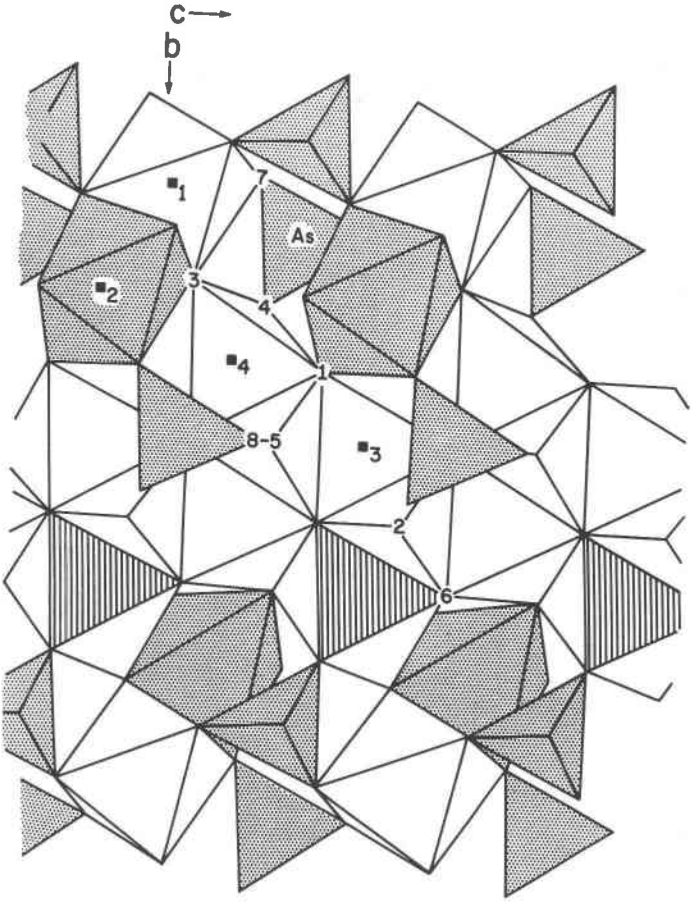

FIG. 1. Portion of the crystal structure of allactite projected down *a**. The sheet is unstippled and between stippled chains of Mn-O octahedra and As-O tetrahedra. Ruled Mn(4)-O faces are shared with Mn(2)-O. When the Mn(2)-O octahedron is placed above the ruled faces, chains running parallel *b* [010] can be seen.

octahedra form an edge-sharing triplet in the A sheet and the remaining Mn(2)-O octahedron shares a face with one of them. The strong repulsion between the Mn(2) and Mn(4) metals results in a distance of 2.974 ±0.007 Å between them and relatively short O-O distances at the common face (O(5)-O(6) 3.01, O(5)-O(4) 2.90, O(4)-O(6) 2.92±0.05 Å).

The abnormally long Mn(2)-O(5) distance suggests a likelihood of five-coordinated Mn^{2+}-O polyhedra. Five-coordinated Mn^{2+} seems to be relatively rare among minerals although a new mineral from Långban, Sweden—eveite, $Mn_2(OH)(AsO_4)$—was shown to be isostructural with

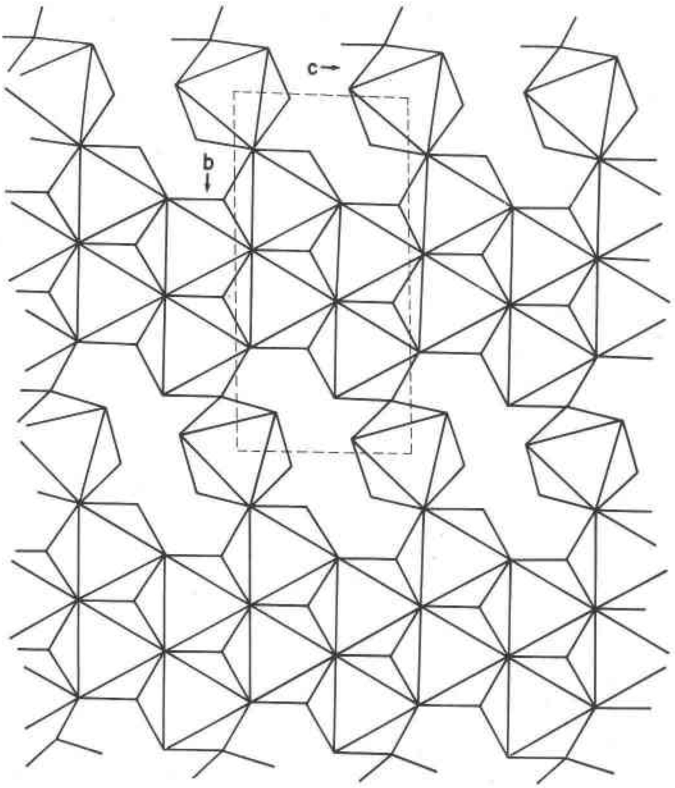

FIG. 2. The sheet in allactite down a^*, slightly idealized.

adamite, $Zn_2(OH)(AsO_4)$ (Moore, 1968). The five-coordinate character of half the Zn^{2+} atoms in adamite has been established (Kokkoros, 1937). It must be stated, however, that the unusual arrangement of cations about the Mn(2)-O octahedron probably induces the long Mn(2)-

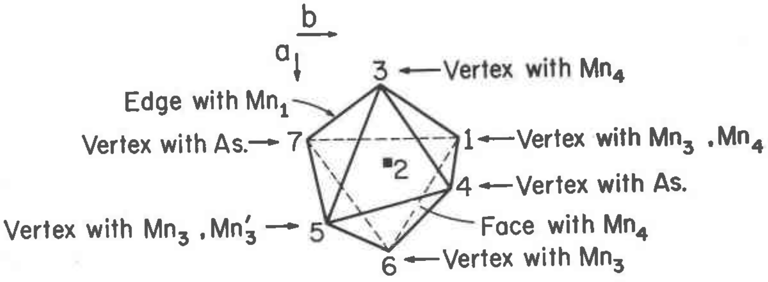

FIG. 3. The Mn(2)-O octahedron down c^* and its immediate neighborhood.

TABLE 4. ALLACTITE. ELECTROSTATIC VALENCE STRENGTHS

[a]O(1)	Mn(2)+Mn(4)+Mn(3)	1.0
O(2)	As+Mn(3)+Mn(3′)+Mn(4)	2.2
[a]O(3)	Mn(4)+Mn(1)+Mn(2′)	1.0
O(4)	As+Mn(4)+Mn(2′)	1.7
[a]O(5)	Mn(2′)+Mn(3)+Mn(3′)+Mn(4)	1.3
[a]O(6)	Mn(2′)+Mn(4)+Mn(3)	1.0
O(7)	As+Mn(2′)+Mn(1)	1.7
O(8)	As+Mn(1)	1.6

[a] Hydroxyl groups.

O(5) distance by cation-cation repulsion so that the Mn(2)-O octahedron is not truly five-coordinated.

The pyrochroite fragment in the allactite sheets is slightly distorted with Mn(3)-Mn(4) 3.30, Mn(3)-Mn(4′) 3.19, Mn(3)-Mn(4″) 3.30, Mn(3)-Mn(3′) 3.19 and Mn(3)-Mn(3″) 3.27±0.007 Å, giving a mean of 3.27 Å. This value should be compared with $a=3.315$ Å reported by Klingsberg and Roy (1959) for pyrochroite, the translation distance between two metals in the plane of the sheet. This shortening in allactite is probably due to the presence of more tightly bound $O^{=}$ ions associated with the arsenate groups combined with repulsion from As and Mn(2) around, above, and below the pyrochroite fragment.

The As-O tetrahedral distances range from 1.65 to 1.72±0.03 Å, the average being 1.68 Å. As observed by Ghose, Fehlmann, and Sundaralingam (1956) for the crystal structure of clinoclase, the As-O distances deviate considerably from regularity. Akin to that structure, there are two 'short' bonds of 1.65 Å and two 'long' bonds of 1.71 Å compared with 1.68 and 1.73 Å for clinoclase. The longest distance, As-O(2) is consistent with the values in Table 4, where O(2) is the only oversaturated oxygen atom associated with the tetrahedral group. In fact, it is seen that the Mn(3)-O(2) 2.29, Mn(3)-O(2′) 2.23, Mn(4)-O(2) 2.30±0.03 Å are all longer than average.

Though only two other basic manganese arsenate structures, flinkite and retzian, are reported in the literature (Moore, 1967), evidence is accumulating which strongly indicates that this mineral group is derivative of pyrochroite fragments. In flinkite, $Mn_2^{2+}Mn^{3+}(OH)_4(AsO_4)$, the pyrochroite sheet character is quite pronounced, with octahedral voids allowing for sheet-bridging AsO_4^{-3} groups. I have just completed the crystal structure analyses of chlorophoenicite, $Mn_3Zn_2(OH)_4[(AsO_4)\cdot(H_4O_4)]$, and the closely related gageite, $(Mn,Mg)_7(OH)_6(O)(SiO_3OH)_2$, both of which are built of pyrochroite fragments, and in forthcoming papers these two structures shall be discussed along with the crystal chemistry of basic manganese arsenates in general.

ACKNOWLEDGEMENTS

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